Clay Mineral: Radiological Characterization

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Abstract. Since the early days, clays have been used for therapeutic purposes. Nowadays, most minerals applied as anti-inflammatory, pharmaceutics and cosmetic are the clay minerals that are used as the active ingredient or, as the excipient, in formulations. Although their large use, few information is available in literature on the content of the radionuclide concentrations of uranium and thorium natural series and ^{40}K in these clay minerals.
The objective of this work is to determine the concentrations of ^{238}U, ^{232}Th, ^{226}Ra, ^{228}Ra, ^{210}Pb and ^{40}K in commercial samples of clay minerals used for pharmaceutical or cosmetic purposes. Two kinds of clays samples were obtained in pharmacies, named green clay and white clay.
Measurement for the determination of ^{238}U and ^{232}Th activity concentration was made by alpha spectrometry and gamma spectrometry was used for ^{226}Ra, ^{228}Ra, ^{210}Pb and ^{40}K determination. Some physical-chemical parameters were also determined as organic carbon and pH. The average activity concentration obtained was 906 ± 340 Bq kg^{-1} for ^{40}K, 40 ± 9 Bq kg^{-1} for ^{226}Ra, 75 ± 9 Bq kg^{-1} for ^{228}Ra, 197 ± 38 Bq kg^{-1} for ^{210}Pb, 51 ± 26 Bq kg^{-1} for ^{238}U and 55 ± 24 Bq kg^{-1} for ^{232}Th, considering both kinds of clay.

Keywords: Radionuclides, clay mineral, pharmaceutical, cosmetic.
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1. INTRODUCTION

Clay minerals are used in pharmaceutical formulations as active ingredient or excipient. As active principles clay minerals are used in oral applications as gastrointestinal protectors, osmotic oral laxatives, antidiarrhoeaics. Topical application includes their use in dermatological protectors and cosmetics. It is also used in spas and aesthetic medicine[1].

The properties for which they are used are fundamentally: a high specific area and adsorptive capacity, rheological properties and chemical inertness.

A fundamental property that must be observed for the use of a material in pharmaceutical formulations is its low or null toxicity. The presence of some elements, even in trace quantities can offer a potential threat for the patient. It is well known that clay mineral, due to its high specific area and ion exchange capability[2], possess a great adsorptive capacity which can cause the accumulation of trace elements such as radionuclides. Little or no information are available in literature on the content of the radioactive elements in clay minerals used for pharmaceutical purposes. In this work eight samples of medicinal clay bought in pharmacies and one with no trade mark were analyzed for their content of ^{238}U, ^{232}Th, ^{226}Ra, ^{228}Ra, ^{210}Pb and ^{40}K. According to their organoleptic characteristics, clays were classified as white clay (AB 1, 2, 3 4 and 5) and green clay (AV 1, 2, 3 and 4). The sample with no trade mark was named AB3.

2. EXPERIMENTAL

Alpha spectrometry were used for the determination of the nuclides ^{238}U and ^{232}Th. Approximately 0,5g of the sample was weighed, spiked with ^{232}U and ^{229}Th and dissolved with a heated aqua regia mixture. The solution was neutralized with NH_4OH till the iron-hidroxide precipitation. Precipitate was dissolved with concentrated HCl, evaporated almost to dryness and re-dissolved in HCl 9 mol L^{-1}. The obtained solution was passed through a pre-conditioned anionic exchange resin column in HCl 9 mol L^{-1} media. The eluate was evaporated to dryness and re-dissolved with HNO_3 8 mol L^{-1}, and passed through a pre-conditioned anionic exchange resin column in HNO_3 8 mol L^{-1} media. Both, U and Th were eluated with HCl 0,1 mol L^{-1}, evaporated and electroplated in a steel disk during one hour using NH_4Cl as electrolyte[3]. The detection of alpha particles was done with a silicon barrier detector and count rates determined during 80,000 seconds.

Activity concentrations of Ra-226, Ra-228, Pb-210 and K-40 were measured in sediment samples by gamma spectrometry with a hyper-pure germanium detector, GEM–15200, from EG&G Ortec. The detector was calibrated using natural soil, rock and water spiked with radionuclides certified by Amersham. Samples were packed in 100 cm^3 cans and sealed for about four weeks prior to the measurement in order to ensure that equilibrium has been reached between Ra-226 and its decay products of short half-life. The Ra-226 activities were determined by taking the mean activity of three separate photopeaks of its daughter nuclides: Pb-214 at 295 keV and 352 keV, and Bi-214 at 609 keV. The Ra-228 content of the samples was determined by measuring the intensities of the 911 keV and 968 keV gamma-ray peaks from Ac-228. The concentration of Pb-210 was carried out by measuring the activity of its low energy peak (47 keV). Self-absorption correction was applied since the attenuation for low energy gamma rays is highly dependent upon sample composition. The approach used was that suggested by Cutshall[4].

3. RESULTS AND CONCLUSIONS

Table 1 shows the obtained results for ^{238}U, ^{232}T, ^{226}Ra, ^{228}Ra, ^{210}Pb and ^{40}K activities concentration, pH and organic carbon (CO). White clays present low content of CO and a wide range of pH while green clays present a more constant pattern for these parameters. Table 2 shows the mean values, standard deviation and variation coefficient for the results obtained for radionuclides determination. It can be seen that green clays are characterized by the higher content of radionuclides, presenting a narrower variation. White clay presents a great variation mainly in its content of U, Th and K.

TABLE 1 – Activity concentrations of ^{238}U, ^{232}T, ^{226}Ra, ^{228}Ra, ^{210}Pb and ^{40}K (Bq/kg), pH and organic carbon (CO) in the analyzed samples

	U-238	*Th-232*	*Ra-226*	*Ra-228*	*Pb-210*	*K-40*	*pH*	*CO*
AB1	123±15	46±2	38±3	64±5	218±17	952±76	7.74	0.10
AB2	68±10	45±2	32±3	70±6	188±15	828±66	8.10	0.05
AB3	117±14	40±2	54±4	82±7	252±20	1069±86	5.68	0.12
AB4	61±10	74±4	27±2	64±5	144±11	76±6	6.04	0.02
AB5	58±10	111±5	32±3	92±7	162±13	758±61	4.57	0.12
AV1	134±19	81±4	51±4	72±6	252±20	1146±92	6.98	0.71
AV2	168±23	92±4	42±3	77±6	198±16	1126±90	6.12	0.57
AV3	188±24	77±4	42±3	76±6	167±13	1114±89	6.97	0.86
AV4	136±18	72±3	40±3	80±6	189±15	1088±87	6.95	0.69

White clay is more enriched in ^{228}Ra over ^{226}Ra than green clay and ^{228}Ra presents a pronounced enrichment over its parent nuclide, Th-232. AB4 and AB5 samples show an enrichment of Th over U compared to the other samples. All samples presented ^{210}Pb activity concentration higher than ^{226}Ra probably due to the great solubility of the later.

TABLE 2 – Mean values, standard deviation (S.D.) and coefficient of variation (C.V.) of the analyzed nuclides in Bq kg^{-1}

	U-238	Th-232	Ra-226	Ra-228	Pb-210	K-40
			white clay			
Mean	85	63	37	74	193	737
S. D.	32	30	10	12	43	388
V. C.	37	47	29	17	22	53
			green clay			
Mean	157	81	44	76	202	1119
S. D.	26	9	5	3	36	24
C. V.	17	11	11	4	18	2

As a comparison the concentration, in Bq kg^{-1}, of ^{238}U, ^{232}Th, ^{226}Ra and ^{40}K found in soil are in the range 16 – 60; 11 – 64; 17 – 60 and 140 – 850[5], respectively. Reference values for intake of some kind of foods are presented in table 3. As no reference values for radionuclides were found for the application of clay mineral as pharmaceutical, the mean values for the analyzed elements in some foods presented in a normal diet[6], were also presented. The levels of radionuclides analyzed in this study present higher concentrations than that generally found in soil worldwide and much higher than that presented in the day-to-day diet.

Compared with mud used in spas the concentration of ^{226}Ra in the present samples is lower than that found in literature, on the other hand, concentrations of ^{232}Th, ^{228}Ra and ^{40}K are of the same order of that found for the so called "radioactive mud"[7].

TABLE 3 – Reference values for meat, grains and vegetables found in diary diet in mBq kg^{-1}

	^{238}U	^{226}Ra	^{210}Pb	^{232}Th	^{228}Ra
Meat	2	15	80	1	10
Grain	20	80	50	3	60
Vegetable*	3	30	30	0,5	20

* Root vegetables and fruits

4. CONCLUSIONS

The content of radionuclides was determined in nine different commercial clay minerals. The average concentration obtained was 906 ± 340 Bq kg^{-1} for ^{40}K, 40 ± 9 Bq kg^{-1} for ^{226}Ra, 75 ± 9 Bq kg^{-1} for ^{228}Ra, 197 ± 38 Bq kg^{-1} for ^{210}Pb, 51 ± 26 Bq kg^{-1} for ^{238}U and 55 ± 24 Bq kg^{-1} for ^{232}Th, considering both kinds of clays. Green clay present higher concentrations than that called white clay. As clay minerals are used in pharmaceutical formulations and in cosmetics, the obtained results show that its content of radionuclides is not insignificant and deserves further investigations.

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